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PREPARATION AND CHARACTERISATION OF CROSS-LINKED SAGO STARCH PHOSPHATES

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PREPARATION AND CHARACTERISATION OF CROSS-LINKED SAGO STARCH PHOSPHATES

By

FARIDAH BINTI HUSSIN

Thesis Submitted in Fulfillment of the Requirements for the Degree of Master of Science in the Faculty of Food Science and Biotechnology Universiti Putra Malaysia

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LIST OF ABBREVIATIONS

AGU	Anhydroglucose unit
BU	Brabender unit
^{o}C	degree Centigrade
DS	Degree of Substitution
dsb	dry starch basis
gm	gram
hr	hour
M	Molar
min	minute (s)
ml	milliliter
nm	nanometer
P	Phosphorus
CFR	Code of Federal Regulation
SIRIM	Standard and Industrial Research Institute of Malaysia
STMP	Sodium trimetaphosphate
STPP	Sodium tripolyphosphate
UV	Ultra Violet
VIS	Visible
µm	micrometer
<	less than
%	percent

Abstract of Thesis Presented to the Senate of Universiti Putra Malaysia in Fulfillment of the Requirements for the Degree of Master of Science.

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BY

FARIDAH HUSSIN

September, 1998

Supervisor : Sharifah Kharidah Bte Syed Muhammad, Ph. D.

Faculty : Food Science and Biotechnology

This project was conducted to study the production of cross-linked sago starch phosphate and to characterise the material produced. Sago starch was phosphorylated at various pHs (from 6 to 11) under a range of phosphate salt concentrations (sodium tripolyphosphate [STPP] [1 to 9%] and sodium trimetaphosphate [STMP] [1 to 4%]) and in the presence of various sodium sulfate concentrations (1 to 9%). The phosphorylation was carried out for 40 to 80 mins at temperatures varying from 27 to 50°C and heating time from 0.5 to 3 hrs at temperatures between 100 to 160°C. It was observed that the reaction pH and concentration of phosphate salts played a significant effect on the phosphorus (P) content, pasting profile, and paste clarity of the sago starch phosphates produced. The phosphorus content was found to increase as the pH and concentration of phosphate salts were increased under all conditions. However, the phosphorus contents were found to be below the standard (STPP [0.4%], STMP [0.04%], and a mixture of STPP and STMP [0.4%]), except when the concentration of STMP was above 1%. The pasting profile showed that at pH 9.5, treatment of sago starch with a

mixture of 5% STPP and 2% STMP yielded the best cross-linked sago starch phosphate where it showed the lowest hot paste viscosity and the highest cold paste viscosity. Paste clarity measurements of the phosphorylated starches indicated that cross-linking had accelerated rapidly with STMP above pH 8, with STPP above pH 9, and with a mixture of the two above pH 6. Paste clarity measurements also showed that cross-linking began to accelerate at 5% and below STPP, and 2% and below STMP when sago starch was phosphorylated at pH 11 and 8, respectively. Judging from the paste properties, phosphorylation of sago starch at 27°C for 1 hr with a mixture of 5% STPP and 2% STMP at pH 9.5 in the presence of 5% sodium sulfate and then heating at 130°C for 2 hr is recommended. Cross-linked sago starch phosphate and commercial cross-linked waxy corn starch (Mazaca 3543X and 3544X) showed similar pasting profile. However, cross-linked sago starch phosphate had higher degree of phosphorylation (phosphorus content), degree of substitution, swelling power and solubility, paste clarity and gel strength. The water holding capacity and sediment volumes were similar to one of the cross-linked waxy corn starches (Mazaca 3544X). Morphology studies showed that these modified starches retained their granule shape with minimal degree of starch damage.

Abstrak tesis yang dikemukakan Kepada Senat Universiti Putra Malaysia
Sebagai Memenuhi Syarat Keperluan Untuk Ijazah Sarjana Sains

PENYEDIAAN DAN PENCIRIAN KANJI SAGU IKATAN-SILANG FOSFAT

Oleh

FARIDAH HUSSIN

September, 1998

Penyelia : Sharifah Kharidah Bte Syed Muhammad, Ph. D.

Fakulti : Sains Makanan dan Bioteknologi

Projek ini dijalankan untuk mengkaji penghasilan dan pencirian kanji sagu fosfat ikatan-silang daripada kanji sagu. Kanji sagu telah difosforilasi pada pH yang berbeza (dari 6 ke 11) dengan menggunakan kepekatan garam-garam fosfat yang berbeza (sodium tripolifosfat [STPP] [1 hingga 9%] dan sodium trimetafosfat [STMP] [1 hingga 4%]) dan dengan kehadiran kepekatan sodium sulfat yang berbeza (1 hingga 9%). Fosforilasi telah dijalankan selama 40 hingga 80 minit pada suhu darapada 27 hingga 50°C dan dipanaskan selama 0.5 hingga 3 jam pada suhu diantara 100 hingga 160°C. Didapati paras pH tindakbalas dan kepekatan garam-garam fosfat menunjukkan kesan yang bermakna keatas kandungan fosforus (P), profil kelikatan, dan kejernihan pes kanji-kanji sagu fosfat yang dihasilkan. Kandugan fosforus didapati bertambah apabila pH dan kepekatan garam-garam fosfat bertambah pada semua keadaan. Walaubagaimanapun, kandungan fosforus didapati di bawah paras piawaian (STPP [0.4%], STMP [0.04%], dan campuran STPP dan STMP [0.4%]), kecuali apabila kepekatan STMP melebihi 1%. Profil kelikatan menunjukkan bahawa kanji sagu yang dirawat dengan campuran 5% STPP dan 2% STMP pada pH 9.5 menghasilkan kanji fosfat yang terbaik dimana ia

menunjukkan kelikatan pes panas yang terendah dan kelikatan pes sejuk yang lebih tertinggi. Pengujian kejernihan pes ke atas kanji yang telah difosforilasi menunjukkan bahawa ikatan-silang telah meningkat dengan cepatnya pada pH lebih daripada 8 dengan STMP, lebih daripada 9 dengan STPP, dan lebih daripada 6 dengan campuran kedua-duanya. Pengukuran kejernihan pes juga menunjukkan bahawa ikatan-silang mula bertambah pada 5% STPP dan ke bawah,

dan ke bawah apabila kanji sagu difosforilasikan pada pH 11 dan 8, masing-masing. Merujuk kepada ciri-ciri kelikatan,

difosforilasi pada suhu 27°C selama 1 jam dengan menggunakan campuran 5% STPP dan 2% STMP pada pH 9.5 dengan kehadiran 5% sodium sulfat dan kemudiannya dipanaskan pada suhu 130°C selama 2 jam digunakan. Kanji sagu fosfat ikatan-silang dan kanji jagung berlilin ikatan silang (Mazaca 3543X dan 3544X) menunjukkan profil kelikatan yang sama. Walaubagaimanapun,

ikatan silang menunjukkan darjah fosforilasi (kandungan fosforus),

penggantian, kuasa pengembangan dan kelarutan, kejernihan pes dan kekuatan gel yang lebih tinggi. Kapasiti pegangan air dan isipadu mendapan adalah sama dengan salah satu daripada kanji-kanji jagung berlilin ikatan silang (Mazaca 3544X). Kajian morfologi menunjukkan kanji-kanji yang telah diubahsuai ini tidak berubah bentuk granul asalnya dengan darjah kerosakan yang rendah.

CHAPTER 1

GENERAL INTRODUCTION

Cross-linked starches are those products resulting from an intentional reaction of starch with bi- or polyfunctional reagents, which will effect a bond between glucose units on separate chains. They are widely used as thickening agents in sauces and dressing, bakery products, puddings, desserts and custards, soups, and emulsifying agent in many food systems, antiblocking dusting agent, warp sizing of denims and surgical dusting powder in other applications (Swinkels, 1992). The types of cross-linked that are of commercial value are distarch adipates, distarch phosphates, and distarch glycerol. Of these, only distarch phosphates and distarch glycerol are used in making modified food starches (Wurzburg, 1986b). In this study, distarch phosphates will be produced through phosphorylation because it is a method commonly employed for cross-linking starches intended for the food industry and other uses (Koch *et al*., 1982).

Distarch phosphates are produced when a phosphate radical bridges two starch molecules and in consequence the starch granule is inhibited from swelling and rupture on pasting in water (Radley, 1976). A small amount of cross-linking greatly reduces both the rate and the degree of granule swelling and sensitivity of starch pastes to processing conditions.

Starch can be cross-linked by reaction with various inorganic phosphate salts as well as specially developed organic reagents. The U.S. Food and Drug Administration allows starch for use in foods to be modified with sodium trimetaphosphate (residual phosphorus not exceeding 0.04%), sodium trimetaphosphate and sodium tripolyphosphate (residual phosphorus not exceeding 0.4%) and phosphorus oxychloride (maximum allowable treatment is 0.1% on starch) (CFR, 1991).

Cross-linked starches have been produced mainly in United States, Europe, Japan and Australia. These products are mostly derived from corn and tapioca starch. As a result, technical information regarding the manufacturing process and the various processing parameters are based on modifications of these starches (Wurzburg, 1986; Rutenberg and Solarek, 1984; Kerr and Cleveland, 1959)

In Malaysia, modified starches are imported for utilization in the local food industries and other applications. Referring to the statistics on import and re-export of merchandises prepared by the Malaysian Industrial Development Authority (MIDA), from January 1995 to August 1996, this country has imported 31,286,116.63 tonnes of modified starches which is equivalent to RM64,911,550.00. United States, Italy, Thailand, Australia, France and Germany supply these modified starches. To date, there is only one local factory producing commercial cross-linked starch either for local utilization or for export. This factory is producing cross-linked starch using waxy corn starch which is imported from Australia. Therefore, if cross-linked starch can be manufactured using one of the local indigenous starches, this will not only save revenue but also diversify the usage of such starch. One such possible indigenous starch which Malaysia is the largest producer and exporter of is sago starch (Azudin and Lim, 1991).

Sago palm occurs throughout Malaysia and it is substantially common in fresh water swamp areas along some river courses and on peat soils (Othman, 1991). Sago starch which is extracted from sago palm has been produced primarily in Sarawak. The main areas of sago starch production in Sarawak are Mukah, Dalat and Igan of the Sibu division. During the last decade, Sarawak has been exporting about 25,000 - 30,000 tonnes of sago starch annually to Peninsular Malaysia, Singapore, Japan and other parts of the world. This monopoly is basically due to the well established sago cultivation areas available and the large scale production of sago starch practiced in this state (Zulpilip *et al*., 1991). In addition, over the past five years there has been a tremendous improvement in starch extraction and processing technology producing high quality sago starch. Azudin *et al*. (1989) in their evaluation of the local starch have shown that sago starch produced by the modern sago factories are well above the quality specifications of the Standard and Industrial Research Institute of Malaysia (SIRIM) standards for sago starch.

Sago starch has been utilized mainly in the production of ‘bee hoon’ (or vermicelli), manufacture of monosodium glutamate, glucose, maltose, dextrose, and fish and prawn crackers (Zulpilip *et al.*, 1991). There has been no report or literature on the suitability of sago starch for the production of modified starch especially cross-linked starch. Therefore, the objectives of this study were:

1. To establish the optimum conditions for phosphorylating sago starch
2. To determine the physico-chemical characteristics of the cross-linked sago starch, and to compare them with that of commercial cross-linked waxy corn starches

CHAPTER 2

LITERATURE REVIEW

Modified Starches

Modified starch is a native starch treated in such a way as to modify one or more of its original physical or chemical properties (Swinkels, 1992). Modification is carried out because unmodified starches cannot be tailored-made and very often are not the best product in a particular application or process as swell with ease and rupture with minimum abuse to produce weak-bodied, cohesive pastes or undesirable gels (Wurzburg, 1986a). The main disadvantages of unmodified starches are shown in Table I.

Modifications of native starches are carried out in order to overcome these disadvantages and thus expand the usefulness of starch for a great number of industrial applications (Wurzburg, 1986a). They are designed to change and improve one or more of the properties as appropriate for a specific application (IFI, 1993) (Table 2).

Table 1: Disadvantages of unmodi

1. **Inconsistent viscosity**. Due to the effects of climat condition of the plant.
2. **Susceptibility to acid attack**. Many food are acid food product made using an unmodified starch wil unmodified starch is degraded by the acid hydrolysis
3. **Susceptibility to shear.** An unmodified starch wi viscosity due to the mechanical action of stirring. T the viscosity of the final product depending upon ho been stirred.
4. **Set-back and syneresis**. In solution the hydro increases with time as thermal motion brings variou close enough proximity for further hydrogen bondin as a colloidal sol 'sets back' into a gel on standing. the process continues with occluded water molecule gel to leave a rubbery solid surrounded by the expre accelerated if the product is frozen then thawed.
5. **Solubility.** A problem arises in any process requirin content due to the limit on the amount that can be 'di as a colloid, imposed by the macromolecular nature

Source : Rothwell and Garner (1986)